Research Paper

Biodiesel from canola oil using a 1 : 1 molar mixture of methanol and ethanol*

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Canola oil was transesterified using a 1 : 1 molar mixture of methanol and ethanol (M/E) with potassium hydroxide (KOH) catalyst. The effects of catalyst concentration (0.5–1.5 wt-%), molar ratio of M/E to canola oil (3 : 1 to 20 : 1) and reaction temperature (25–75 °C) on the percentage yield measured after 2.5 and 5.0 min were optimized using a central composite design. A maximum percentage yield of 98% was obtained for a catalyst concentration of 1.1 wt-% and an M/E to canola oil molar ratio of 20 : 1 at 25 °C at 2.5 min, whereas a maximum percentage yield of 99% was obtained for a catalyst concentration of 1.15 wt-% and all molar ratios of reactants at 25 °C at 5 min. Statistical analysis demonstrated that increasing catalyst concentration and molar ratio of reactants resulted in curvilinear and linear trends in percentage yield, both at 2.5 and 5 min. However, reaction temperature, which affected the percentage yield at 2.5 min linearly, was insignificant at 5 min. The resultant mixed methyl/ethyl canola esters exhibited enhanced low-temperature performance and lubricity properties in comparison to neat canola oil methyl esters and also satisfied ASTM D6751 and EN 14214 standards with respect to oxidation stability, kinematic viscosity, and acid value.

1 Introduction

Biodiesel is defined chemically as simple monoalkyl esters (typically methyl or ethyl) of long-chain fatty acids, which meet ASTM and EN specifications. Biodiesel is produced from the transesterification of vegetable oils and animal fats. The advantages of biodiesel over conventional petroleum diesel fuels are its domestic origin, derivation from a renewable feedstock, biodegradability, non-toxicity, cleaner emissions, superior lubricating properties, and the ability to be blended in any proportion with petroleum diesel. Biodiesel is typically produced using methanol, resulting in fatty acid methyl esters (FAME). However, methanol is derived commercially from petrochemical processes and yields biodiesel with relatively poor low-temperature performance [1–5] and reduced lubricity [1, 2] in comparison to biodiesel produced from higher alcohols. Biodiesel obtained from ethanolysis of triacylglycerols (TAG), yielding fatty acid ethyl esters (FAEE), is completely bio-derived, since ethanol may be obtained from various biomass sources, such as corn and sugarcane. However, ethanol is currently more expensive than methanol, and recent studies [1, 2] have indicated that the kinematic viscosity of FAEE is slightly higher than that of FAME, but still normally within specifications.

In a previous study, various mixtures of methanol and ethanol in the presence of KOH were used to transesterify canola oil [1]. The results indicated that canola oil methyl esters (COME) had poorer lubricity compared to canola oil

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ethyl esters (COEE). The synthesis of COEE, however, was complicated by an inadequate separation of the COEE phase from the glycerol phase [1]. Accordingly, mixtures of methanol and ethanol were investigated and the following advantages were elucidated: The rate of transesterification was improved [1], better lubricity was obtained than from methyl esters alone [1], and better phase separation was achieved when compared to using only ethanol [6, 7].

The aim of the current investigation was to optimize the experimental conditions of ester production from canola oil employing a 1 : 1 molar mixture of methanol and ethanol with KOH as catalyst using response surface methodology, which is hitherto unreported. A central composite design with eight factorial points, six replicated center points and six axial points was used to study the effects of catalyst concentration (wt-%), molar ratio of M/E to canola oil, and reaction temperature (°C) on the percentage of conversion to esters after 2.5 and 5.0 min. Additionally, the resultant mixture of COME and COEE was analyzed with respect to low-temperature performance, lubricity, kinematic viscosity, oxidation stability, and acid value, and was compared to neat COME and COEE using ASTM D6751 [8] and EN 14214 [9] standards.

2 Materials and methods

2.1 Materials and apparatus

Canola oil was obtained commercially and found to contain by GC [10] palmitic (4.1 wt-%), oleic (61 wt-%), linoleic (21 wt-%), and linolenic acid (8.8 wt-%), with trace amounts of arachidic, behenic, myristic, palmitoleic, stearic, linolenic, erucic and lignoceric acids. Anhydrous methanol, ethanol (200 proof), and potassium hydroxide were obtained from Fisher Scientific (Somerville, NJ, USA), and care was taken to avoid contact with water that may lower alcoholysis of the canola oil [11]. All other chemicals and reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Each experiment was conducted in a 500-mL round-bottom flask connected to a reflux condenser and the reaction mixture was agitated by magnetic stirring at 600 rpm, as described previously [12].

2.2 Methods

Esters were produced using M/E and KOH as catalyst, which were first blended according to the calculated amount as per experimental design and then mixed with canola oil. The mixture was heated at the experimental temperature for 2.5 and 5.0 min in two sets of experiments. After the reaction was stopped by addition of oxalic acid [13], the crude mixture was centrifuged at 3000 rpm for 1 min, followed by decantation of the top ester layer. At this stage, a small sample of crude ester was removed for subsequent HPLC determination of unreacted TAG (Section 2.3). The crude ester sample was then washed with distilled water (3 ×) until a neutral pH was achieved, followed by drying with brine (sat. aq.) and $MgSO_4$ to afford alkyl esters. The ratio of methyl to ethyl esters in the final product was determined by ^{1}H-NMR (500 MHz, $CDCl_3$ solvent, Bruker AV-500 spectrometer; Billerica, MA, USA) through comparison of the integration values for the peaks corresponding to the methyl ester protons of COME and the methylene protons of the ethyl esters of COEE, which was found to be 2.7 : 1 (methyl/ethyl esters) under the optimum conditions determined in this study at 5 min.

2.3 HPLC analyses

The esters were analyzed using an RP-HPLC system equipped with an ELSD detector set at 40 °C. A 1 : 15 dilution of biodiesel in dichloromethane was used for the analysis. A Shimadzu HPLC system equipped with EZstart 7.2.1 software and an Altech HP prevail C18 column of length 150 mm and inner diameter 4.6 mm was used. The mobile phase was a mixture of acetonitrile and dichloromethane, with a gradient of dichloromethane maintained to separate constituents in the ester sample [14]. The following gradient was maintained: gradient time: 0, 15, 30, 32, 35 min; % dichloromethane: 0, 15, 70, 70, 0, respectively. A flow rate of 1.0 mL/min was maintained for the mobile phase. A sample volume of 10 μL and a gain of 5 were set for each of the runs. Using this method, FAME and FAEE were separated based on their selective retention according to their polarity.

2.4 Calculation of percentage yield

Percentage yield was calculated by using the following equation:

$$\% \text{ yield} = \frac{(A_{FAME} + A_{FAEE}) \times 100}{A_{FAME} + A_{FAEE} + A_{TG} + A_{DG} + A_{MG}},$$

where $A_{FAME} = A_b + f_1 A_d + f_2 A_f + f_3 A_h$ and $A_{FAEE} = f_4 A_c + f_5 A_e + f_6 A_g + f_7 A_i$. A_b, A_c, A_d, A_e, A_f, A_g, A_h and A_i were the areas under peaks b, c, d, e, f, g, h and i respectively (Fig. 1). A_{TG}, A_{DG}, and A_{MG} were the areas representing triacylglycerols, diacylglycerols and monoacylglycerols, respectively. The response factors for methyl linoleate, methyl oleate, methyl palmitate, ethyl linolenate, ethyl linoleate, ethyl oleate and ethyl palmitate relative to methyl linolenate were f_1, f_2, f_3, f_4, f_5, f_6, and f_7. The response factors were all assumed to be 1 for mono-, di- and triacylglycerols.

2.5 Experimental design

Response surface methodology was used to optimize conversion for three selected factors: catalyst concentration in wt-% (*C*), M/E: canola oil molar ratio (*MR*) and reaction tempera-
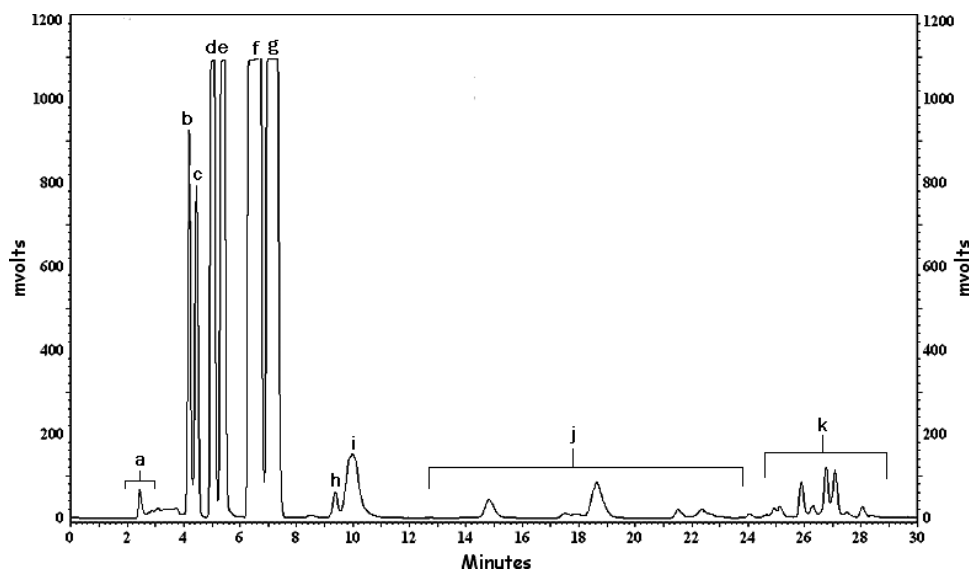
Figure 1. Chromatogram of a mixed canola oil methyl and ethyl ester sample using RP-HPLC. (a) Monoacylglycerols (MG), (b) methyl linolenate (FAME), (c) ethyl linolenate (FAEE), (d) methyl linoleate (FAME), (e) ethyl linoleate (FAEE), (f) methyl oleate (FAME), (g) ethyl oleate (FAEE), (h) methyl palmitate (FAME), (i) ethyl palmitate (FAEE), (j) diacylglycerols (DG), (k) unreacted triacylglycerols present in the mixed ester sample.

ture (*T*) in °C [15]. The selection of factor levels was based on previous research and practical considerations [16]. The upper temperature level (75 °C) was just below the boiling point of ethanol, and the lower level (25 °C) was room temperature. Catalyst concentration extremes (0.5 and 1.5 wt-%) were based on literature data [15]. The lower molar ratio (3 : 1) was the minimum amount of alcohol required from the reaction stoichiometry, and the upper molar ratio (20 : 1) was based on previous research [12]. In a previous study, transesterification of canola oil was performed in the presence of KOH using methanol and ethanol separately [17]. Although not directly stated, tabulated results showed that, for some combinations of catalyst concentration, molar ratio of alcohol (methanol or ethanol) to oil and reaction temperature, yields as high as 98–99% were obtained after 5 min of reaction [17]. Hence, the reaction time was fixed at 2.5 and 5 min in two separate experiments. A central composite design with eight factorial points, six axial points and six replicated center points was used for each study (Table 1). The results obtained from the 20 experimental runs were analyzed using the GLM procedure in Statistical Analysis System (SAS) for Windows, version 9.1 (Cary, NC, USA), to estimate the parameters of a complete second-order model represented by Eq. (1), for the three factors being studied [16, 18],

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum \sum_{i=1<j}^{3} \beta_{ij} x_{ij} \tag{1}$$

and determines the most influential terms using $\alpha = 0.05$.

2.6 Low-temperature properties

Cloud point (CP) and pour point (PP) determinations were made in agreement with ASTM D5773 [19] and ASTM

D5949 [20] using a phase technology analyzer model PSA-70S (Richmond, B.C., Canada). CP and PP are rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Cold filter plugging point (CFPP) was determined in accordance with ASTM D6371 [21] utilizing an ISL automatic CFPP analyzer model FPP 5Gs (Houston, TX, USA). Each sample was run in triplicate and mean values are reported (Table 2).

2.7 Kinematic viscosity

Kinematic viscosity (υ, mm^2/s) was determined with Cannon-Fenske viscometers (Cannon Instrument Co., State College, PA, USA) at 40 °C in accordance with ASTM D445 [22]. All experiments were run in triplicate and mean values are reported (Table 2).

2.8 Lubricity

Lubricity (lub) determinations were performed at 60 °C (controlled to less than ±1 °C), according to ASTM D6079 [23] using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, UK) *via* Lazar Scientific (Granger, IN, USA). Wear scar (μm) values (Table 2) are the average of two replicates, measuring the maximum value of the *x*- and *y*-axis of each wear scar. The average wear scar diameter of each replicate was determined by calculating the average of the *x*- and *y*-axis wear scar lengths.

2.9 Oxidation stability

Oil stability index (OSI, h) was measured in accordance with EN 14112 [24] employing a Rancimat model 743

Table 1. Central composite design for transesterification of canola oil with a 1:1 mole mixture of methanol and ethanol.[†]

Central composite design component	Factor			% Yield	
	C	MR	T	at 2.5 min	at 5 min
Factorial points	0.7	7.3 : 1	35	77.24	85.51
	1.3	7.3 : 1	35	92.52	96.88
	0.7	16.7 : 1	35	88.28	89.36
	1.3	16.7 : 1	35	96.40	97.11
	0.7	7.3 : 1	65	83.42	86.05
	1.3	7.3 : 1	65	98.70	98.93
	0.7	16.7 : 1	65	88.74	90.61
	1.3	16.7 : 1	65	95.86	97.54
Axial points	0.5	12 : 1	50	73.06	80.35
	1.5	12 : 1	50	94.71	95.25
	1.0	3 : 1	50	90.45	93.87
	1.0	20 : 1	50	98.18	98.41
	1.0	12 : 1	25	91.53	96.92
	1.0	12 : 1	75	97.10	97.87
Center points	1.0	12 : 1	50	96.52	98.22
	1.0	12 : 1	50	94.48	94.98
	1.0	12 : 1	50	93.42	95.11
	1.0	12 : 1	50	95.92	96.66
	1.0	12 : 1	50	94.74	96.43
	1.0	12 : 1	50	95.90	97.26

[†] *C*, Catalyst concentration (wt-%); *MR*, molar ratio of M/E to canola oil; *T*, reaction temperature (°C).

Table 2. Characterization of optimized COME, COEE, and mixtures of COME and COEE (1.3 : 1 and 2.7 : 1), and comparison with ASTM D6751 and EN 14214.

	ASTM D6751	EN 14214	COME	COEE	ME/EE 1.3 : 1[†]	ME/EE 2.7 : 1[‡]
CP [°C]	Report	–	−3 ± 0.3	−5 ± 0.4	−4 ± 0.4	−3 ± 0.4
PP [°C]	–	–	−12 ± 1.2	−14 ± 1.4	−13 ± 1.1	−12 ± 1.2
CFPP [°C]	–	——	−7 ± 0.6	−9 ± 0.7	−8 ± 0.6	−7 ± 0.5
υ [mm^2/s], 40 °C	1.9–6.0	3.5–5.0	4.61 ± 0.01	5.11 ± 0.01	4.69 ± 0.01	4.63 ± 0.01
Lub [μm], 60 °C	–	–	159 ± 3	132 ± 2	146 ± 3	151 ± 2
OSI [h]	3 min	6 min	6.8 (11.6)[§]	7.0 (11.4)[§]	7.1 (11.8)[§]	6.9 (11.5)[§]
AV [mg KOH/g]	0.50 max	0.50 max	0.06 ± 0.01	0.37 ± 0.03	0.35 ± 0.01	0.32 ± 0.02

[†] Classical reaction conditions as described in Section 3.3.1.
[‡] Optimum conditions after 5.0 min of reaction.
[§] After addition of 100 ppm TBHQ; σ ± 0.2 h.
– Not specified in the standard; — specification varies according to country and time of year.

instrument from Metrohm (Herisau, Switzerland). The flow rate of air through 3 ± 0.01 g of sample was 10 L/h. The block temperature was set to 110 °C. The glass conductivity-measuring vessel contained 50 ± 0.1 mL distilled water. Each sample was run in triplicate and mean values (±0.2 h) are reported (Table 2). OSI was mathematically determined as the inflection point of a computer-generated plot of conductivity of distilled water *versus* time.

2.10 Acid value

Acid value (AV, mg KOH/g sample) titrations were performed as described in AOCS Method Cd 3d-63 [25] using a Metrohm 836 Titrando (Westbury, NY, USA) autotitrator equipped with a model 801 stirrer, a Metrohm 6.0229.100 Solvotrode, and Tiamo 1.1 Light software. However, the official method was modified for scale to use 2 g of sample and 0.02 M KOH. The

titration endpoint was determined by the instrument and visually verified using a phenolphthalein indicator. Each sample was run in triplicate and mean values are reported (Table 2).

3 Results and discussion

3.1 Optimization of percent yield at 2.5 min

Table 3 provides the ANOVA summary for the full quadratic model for percentage yield at 2.5 min. Based on $\alpha = 0.05$, terms with p value less than 0.05 significantly affected the percent yield at 2.5 min, and only those terms were included in the final model used to characterize the response surface. It was found that only the β_1 (catalyst concentration linear term), β_2 (molar ratio of M/E to canola oil linear term), β_3 (reaction temperature linear term), β_{11} (catalyst concentration quadratic term), β_{12} (interaction between catalyst concentration and molar ratio of M/E to canola oil) and β_{23} (interaction between molar ratio of M/E to canola oil and reaction temperature) coefficients were significantly different from zero. The reduced response surface model used to describe percent yield at 2.5 min is represented by Eq. (2):

$$\hat{Y} = -11.10 + 126.96 \times C - 45.33 \times C^2 + 2.92 \times MR + 0.36 \times T - 1.35 \times C \times MR - 0.02 \times MR \times T \quad (2)$$

where $\hat{Y}$ is the predicted percentage yield at 2.5 min, C is the catalyst concentration (wt-%), MR is the molar ratio of M/E to canola oil and T is the reaction temperature (°C). All of the factors studied were found to significantly affect percentage yield in the time period studied. A brief discussion of the influential terms follows.

3.1.1 Interaction

Equation (2) includes two significant interaction terms affecting percentage yield at 2.5 min. Since all three factors

were involved in one or both interactions, these factors did not independently affect percentage yield at 2.5 min. The significant $C \times MR$ interaction means that the effect of catalyst concentration on percentage yield at 2.5 min depends on the specific level of the molar ratio of M/E to canola oil and *vice versa*. This can be readily observed in Fig. 2, which provides the fitted response surface generated by Eq. (2) at 50 °C reaction temperature. Likewise, the significant $MR \times T$ interaction means that the effect of temperature on percentage yield at 2.5 min depends on the specific level of the molar ratio of M/E to canola oil and *vice versa*. This can be readily observed in Fig. 3 which provides the fitted response surface generated by Eq. (2) for 1 wt-% catalyst concentration.

3.1.2 Catalyst concentration

Catalyst concentration was a very important factor in the transesterification of canola oil. The relationship between percentage yield at 2.5 min and catalyst concentration was found to be curvilinear with a positive linear coefficient and a negative quadratic coefficient. This suggested that percentage yield at 2.5 min was inhibited by high catalyst concentration, which was consistent with previous studies [12]. This reduction in yield may be because the reverse reaction was favored at high catalyst concentration [26]. As can be seen in Fig. 2, the response surface starts leveling off for catalyst concentrations in the range of 1.03–1.17 wt-% and – for higher molar ratios – decreases as the catalyst concentration increases above 1.17 wt-%. High ester conversion (>90%) was generally obtained for catalyst concentrations in the range of 1.1–1.5 wt-%. Maximum ester conversion of 98% was achieved at a catalyst concentration of 1.1 wt-%.

3.1.3 Molar ratio of M/E to canola oil

The relationship between percentage yield at 2.5 min and molar ratio of M/E to canola oil was linear [12] (Figs. 2, 3). Percentage conversion increased as the molar ratio of M/E to canola oil

Table 3. ANOVA summary for the full quadratic model for percentage yield measured at 2.5 and 5 min.

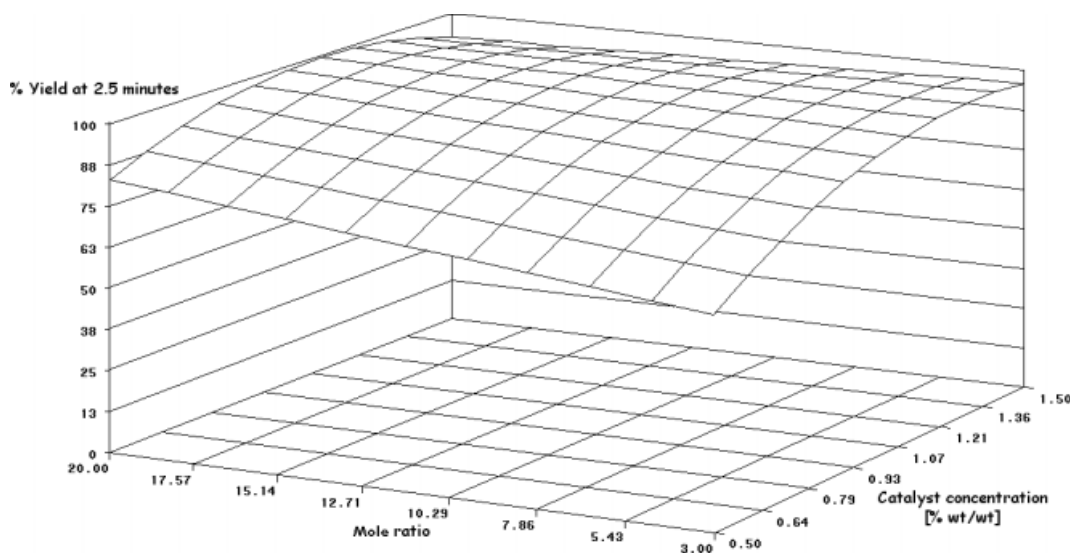| Model term	% Yield at 2.5 min		% Yield at 5 min	
	Mean squares	p value	Mean squares	p value
C (linear)	494.85	<0.0001	299.83	<0.0001
C (quadratic)	239.74	<0.0001	151.26	<0.0001
MR (linear)	67.66	<0.0001	16.22	0.0046
MR (quadratic)	2.18	0.1534	1.20	0.3453
T (linear)	34.31	0.0001	2.52	0.1829
T (quadratic)	2.18	0.1534	0.34	0.6088
$C \times MR$	29.33	0.0002	11.44	0.0123
$C \times T$	0.12	0.7193	0.05	0.8304
$MR \times T$	19.34	0.0010	0.10	0.7778
Residual	0.91		1.23	

Figure 2. Response surface of percentage yield at 2.5 min *vs.* molar ratio and catalyst concentration at 50 °C temperature.

increased when the catalyst concentration was less than 1.1 wt-%, but for higher catalyst concentrations the percent yield decreased as the molar ratio of M/E to canola oil increased. Percentage yield also increased linearly as the molar ratio of M/E to canola oil increased when the reaction temperature was below 70 °C. However, the molar ratio of M/E to canola oil had little effect on percent yield at 2.5 min at higher temperatures.

3.1.4 Reaction temperature

The relationship between percentage conversion and temperature was linear (Fig. 3) [17]. Percentage conversion increased linearly as the reaction temperature increased when the molar ratio of M/E to canola oil was less than 16 : 1, but for higher molar ratios of M/E to canola oil the reaction temperature had little impact on percentage yield at 2.5 min.

From the ANOVA summary for the reduced model for percentage yield at 2.5 min, insufficient evidence for 'lack-of-fit' for the reduced model ($p = 0.7393$) indicated that the model adequately characterized the relationship between the three influential factors (catalyst concentration, molar ratio of M/E to canola oil, and reaction temperature) and percentage yield at 2.5 min. Furthermore, the coefficient of determination for the model was high ($R^2 = 0.99$). A maximum percentage yield of 98% was predicted for a catalyst concentration of 1.1 wt-% and a molar ratio of M/E to canola oil of 20 : 1 at a reaction temperature of 25 °C.

3.2 Optimization of percent yield at 5 min

Table 3 provides the ANOVA summary for the full quadratic model for percentage yield at 5 min. Based on $\alpha = 0.05$, only

terms with p values less than 0.05 significantly affected percent yield at 5 min, and hence only those terms were included in the final model used to characterize the response surface. The reduced response surface model used to describe percent yield at 5 min is represented by Eq. (3):

$$\hat{Y} = 31.99 + 97.48 \times C - 35.88 \times C^2 + 1.07 \times MR - 0.84 \times C \times MR \tag{3}$$

where $\hat{Y}$ is the predicted percentage yield at 5 min (C and MR as above). It was found that only β_1, β_2, β_{11} and β_{12} were significantly different from zero. All terms containing temperature were found to be insignificant; thus, temperature did not significantly affect percentage yield at 5 min. This result is in agreement with previous work that used other oil sources [12]. However, the time required to reach maximum conversion decreased as temperature increased. A brief discussion of the influential terms follows.

3.2.1 Interaction

The significant interaction term for catalyst concentration and molar ratio of M/E to canola oil indicated that these two factors did not independently affect percentage yield at 5 min. Thus, the effect of one factor on percentage yield at 5 min depended on the specific level of the other factor. This can be readily observed in Fig. 4 which provides the fitted response surface generated by Eq. (3).

3.2.2 Catalyst concentration

The relationship between percentage yield at 5 min and catalyst concentration was found to be curvilinear with a positive
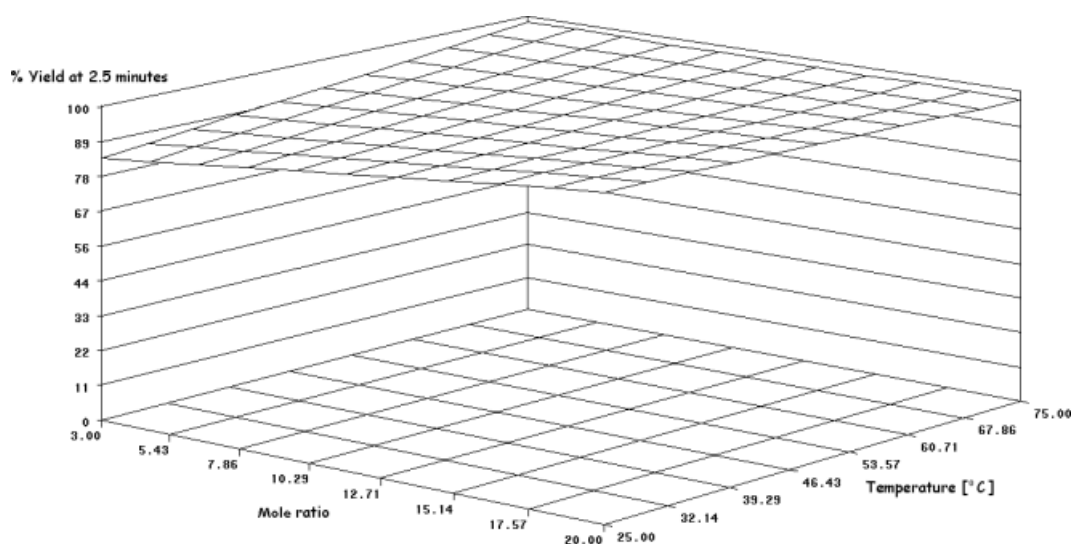
Figure 3. Response surface of percentage yield at 2.5 min *vs.* molar ratio and temperature for 1 wt-% catalyst concentration.

linear coefficient and a negative quadratic coefficient. This suggested that percent yield at 5 min was inhibited at high catalyst concentration, which was consistent with prior studies [12]. This inhibition in yield may be because the reverse reaction was favored at high catalyst concentrations [26]. As can be seen in Fig. 4, the response surface starts to level off for catalyst concentrations in the range of 1.07–1.21 wt-% and, for higher molar ratios of M/E to canola oil, decreases as the catalyst concentration increases above 1.21 wt-%. High ester conversion (>90%) was generally obtained for catalyst concentrations in the range of 1.21–1.5 wt-%, and yields were only slightly higher than those obtained after 2.5 min of reaction time. Maximum ester conversion of 99% was obtained for 1.15 wt-% catalyst concentration. Essentially, at 5.0 min, the reaction had proceeded further to completion with a catalyst concentration of 1.21 to 1.5 wt-% in comparison to 2.5 min.

3.2.3 Molar ratio of M/E to canola oil

The molar ratio of M/E to canola oil also influenced the transesterification of canola oil. The relationship between percentage yield at 5 min and molar ratio of M/E to canola oil was linear [12] (Fig. 4). Percentage yield increased linearly as the molar ratio of M/E to canola oil increased when the catalyst concentration was less than ~1.15 wt-%, but decreased as the molar ratio of M/E to canola oil increased at higher catalyst concentrations.

From the ANOVA summary for the reduced model for percent yield at 5 min, insufficient evidence for 'lack-of-fit' for the reduced model ($p = 0.7899$) indicated that the model adequately characterized the relationship between the two influential factors, catalyst concentration and molar ratio of M/E to canola oil, and percentage yield at 5 min. Further-

more, the coefficient of determination for the model was large ($R^2 = 0.97$). Since percentage yields were independent of reaction temperature after 5 min, a maximum percentage yield of 99% was predicted for a catalyst concentration of 1.15 wt-% and all molar ratios of M/E to canola oil at a reaction temperature of 25 °C. The best conversions obtained at 2.5 and 5 min required a high molar ratio of M/E to canola oil, which may be cost prohibited. A reduction in the molar ratio of M/E to canola oil along with a slight increase in the amount of KOH could be used to obtain high conversions, and this would positively impact on the economic assessment. From the statistical analysis, it was found that catalyst concentration, molar ratio of M/E to canola oil, and reaction temperature, all significantly affected the percentage conversion at 2.5 min. However, reaction temperature did not significantly influence percentage conversion at 5 min. Therefore, there was a cut-off time between 2.5 and 5 min beyond which the temperature did not significantly affect conversion. In order to determine the cut-off time, the set of experiments was repeated for 3.3 and 4.2 min. From the ANOVA summary, it was found that the T (linear) and $MR \times T$ terms, which significantly affected conversion at 2.5 min, became insignificant at 5 min. Hence, only these two terms were used to determine the average p value, which was calculated by taking the average of the p values for the T (linear) and $MR \times T$ terms in the percentage yield model. The other temperature terms were insignificant at both 2.5 and 5 min and hence were not taken into consideration when calculating the average p value. The following data was obtained: reaction time: 2.5, 3.3, 4.2, 5.0 min; average p value: 0.00, 0.02, 0.16, and 0.48, respectively. Based on $\alpha = 0.05$, at any time period temperature significantly affected percentage yield only if the average p value was less than 0.05. By interpolation, the cut-off time was found to be about
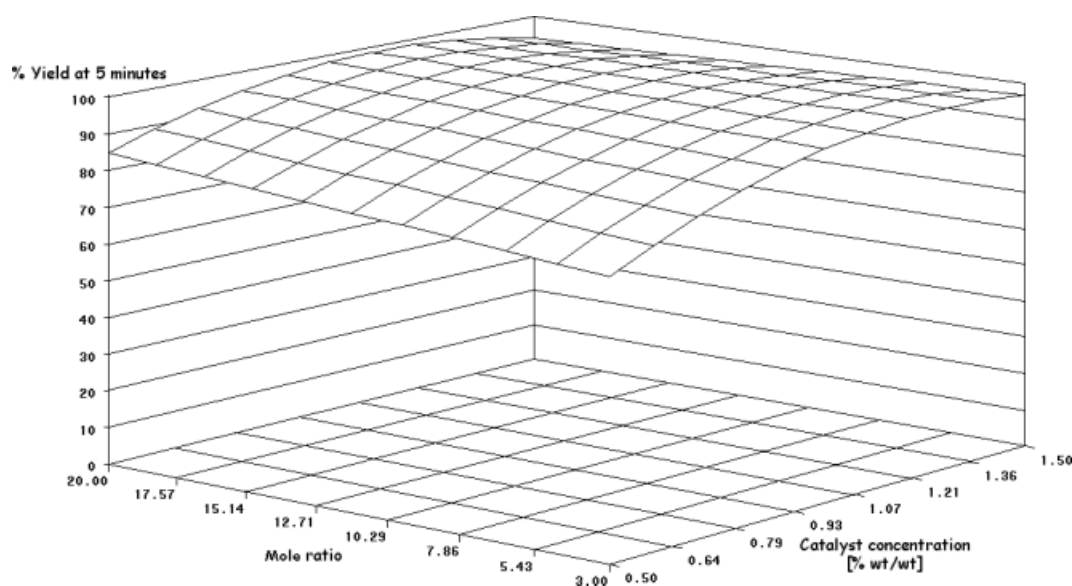
Figure 4. Response surface of percentage yield at 5 min *vs.* catalyst concentration and molar ratio.

3.5 min. Hence, reaction temperature significantly affected percentage yield up to 3.5 min of reaction time, but beyond that temperature had no effect on conversion based on α = 0.05. This result was true over all ranges of catalyst concentration and molar ratio of M/E to canola oil studied.

3.3 Physical and chemical properties

Although not directly measured in the present study, substitution of methyl esters for ethyl esters in biodiesel is known to impart slightly enhanced cetane numbers and heat content, both of which are beneficial to fuel performance in compression-ignition (diesel) engines [27, 28]. Other potential benefits are revealed below, along with a concomitant discussion on the influence of mixed methyl and ethyl esters on the fuel properties of biodiesel resulting from alcoholysis of canola oil with M/E.

3.3.1 Ratio of methyl to ethyl esters

Alcoholysis of canola oil with M/E at room temperature as described in Section 2.2 yielded a methyl-to-ethyl ester ratio of 2.7 : 1, as determined by ^{1}H-NMR spectroscopy. This result is not unexpected since methanolysis proceeds at a faster rate than ethanolysis because of the higher reactivity of methoxide as compared to ethoxide [29]. Repetition of the alcoholysis of canola oil with a 9 : 1 molar ratio of M/E to canola oil and employing classical reaction conditions (70 °C, 60 min, 1.15 wt-% KOH) afforded a methyl/ethyl ester ratio of 1.3 : 1. These results indicated that the methyl ester is preferred at both low (2.7 : 1) and high (1.3 : 1) temperature; however, at high temperature the preference for methyl esters

is diminished. For the sake of the physical property analysis described below, esters resulting from both ratios are described, along with pure COME and COEE.

3.3.2 Low-temperature operability

Replacement of the methyl ester moiety of FAME with that of higher alcohols is known to positively influence low-temperature operability of biodiesel [3, 4, 5, 27, 28]. As expected, COEE exhibited marginally enhanced cold-flow properties in comparison to COME, as evidenced by reduced CP, PP, and CFPP (Table 2). Mixed canola oil methyl and ethyl esters (COME/EE) were found to possess low-temperature properties intermediate between those of pure COME and COEE, with 2.7 : 1 COME/EE more closely mimicking that of pure COME and 1.3 : 1 COME/EE essentially exhibiting values that resemble the mathematical average of COME and COEE results.

3.3.3 Acid value, kinematic viscosity, and lubricity

Acid value (AV) is limited to a maximum value of 0.50 mg KOH/g sample in both ASTM D6751 and EN 14214. All samples were found to satisfy this requirement (Table 2). Kinematic viscosity (υ, 40 °C) is also specified in both ASTM D6751 (1.9–6.0 mm^2/s) and EN 14214 (3.5–5.0 mm^2/s). Substitution of the methyl ester moiety of FAME with that of higher alcohols is known to increase υ [2, 27, 28], which was also observed in the present study (Table 2). In fact, pure COEE exhibited υ (5.111 ± 0.01 mm^2/s) in excess of the EN 14214 requirement but within the ASTM D6751 specification. Esters resulting from M/E at ratios of either 2.7 : 1 or

1.3 : 1, although slightly higher than pure COME, easily satisfied both standard specifications with respect to υ. Lubricity is not specified in either ASTM D6751 or EN 14214 since biodiesel possesses inherently good lubricating properties [2, 27, 30]. Nonetheless, the lubricity-enhancing effect of increasing ester headgroup size on the lubricity of biodiesel has been previously discussed [2], and is confirmed in the present study. Examination of the wear scars produced by HFRR (60 °C, ASTM D6079) revealed that COEE (132 ± 2 μm) displayed enhanced lubricity over COME (159 ± 2 μm; Table 2). COME/EE mixtures also exhibited improved lubricity over pure COME, with the effect being more pronounced in the 1.3 : 1 mixture *versus* the 2.7 : 1 mixture, which is of course attributed to the higher percentage of COEE in the 1.3 : 1 mixture.

3.3.4 Oxidation stability

Biodiesel is considerably more susceptible to autoxidation than conventional petroleum diesel fuel. Consequently, autoxidation is a serious threat to the fuel quality of biodiesel. Both ASTM D6751 and EN 14214 contain an oxidation stability specification, EN 14112, whereby biodiesel must resist oxidation for at least 3 (ASTM D6751) or 6 h (EN 14214). Not only will biodiesel with poor oxidation stability fail relevant specifications, but oxidative degradation negatively affects AV and υ [31], both of which are specified in ASTM D6751 and EN 14214. As can be seen from Table 2, all samples satisfied both ASTM D6751 and EN 14214 requirements. Additionally, treatment of fuels with anti-oxidant additives is ubiquitous in the fuels industry. Therefore, the influence of a common synthetic anti-oxidant, *tert*-butyl-hydroquinone (TBHQ), was of interest. As expected, addition of TBHQ at a relatively low load level (100 ppm) significantly enhanced the oxidative stability of each sample (Table 2).

4 Conclusions

In summary, response surface analysis was performed to assess the effects of potassium hydroxide concentration, molar ratio of M/E to canola oil, and reaction temperature on the percentage yield measured at 2.5 and 5.0 min. From statistical analysis it was found that catalyst concentration, molar ratio of M/E to canola oil, and reaction temperature, all significantly affected the percentage conversion at 2.5 min. However, reaction temperature did not significantly influence percentage conversion at 5.0 min. A cut-off time of about 3.5 min was determined by interpolating the average *p* value and reaction time data. Hence, reaction temperature significantly affected the conversion of canola oil to esters up to 3.5 min and was insignificant thereafter. Lastly, COME/EE mixtures exhibited enhanced low-temperature performance and lubricity properties in comparison to neat COME and also satisfied ASTM D6751 and EN 14214 standards with respect to oxidation stability, kinematic viscosity, and acid value.

Conflict of interest statement

The authors have declared no conflict of interest.

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